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A review of the dehydrocyclodimerization route to preceramic polysilazanes starting from $(CH_3SiHNH)_n$, the ammonolysis product of CH_3SiHCl_2, as well as similar processing of coammonolysis products and the application of the "living" polymer intermediates involved in this chemistry in the preparation of novel hybrid preceramic polymers.

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RECENT DEVELOPMENTS

by

Dietmar Seyferth, G.H. Wiseman, J.M Schwark, Y.-F. Yu and C.A. Poutasse

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ORGANOSILICON POLYMERS AS PRECURSORS
FOR SILICON-CONTAINING CERAMICS:
RECENT DEVELOPMENTS

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INTRODUCTION AND GENERAL COMMENTS

Silicon-containing ceramics include the oxide materials, silica and the
silicates; the binary compounds of silicon with non-metals, principally silicon
carbide and silicon nitride; silicon oxynitride and the sialons; main group and
transition metal silicides, and, finally, elemental silicon itself. There is a
vigorous research activity throughout the world on the preparation of all of
these classes of solid silicon compounds by the newer preparative techniques.
In this report, we will focus on silicon carbide and silicon nitride.

Silicon carbide, SiC [1] and silicon nitride, Si_3N_4 [2], have been known
for some time. Their properties, especially high thermal and chemical stability,
hardness, high strength, and a variety of other properties have led to useful
applications for both of these materials.

The "conventional" methods for the preparation of SiC and Si_3N_4, the
high temperature reaction of fine grade sand and coke (with additions of
sawdust and NaCl) in an electric furnace (the Acheson process) for the former
and usually the direct nitridation of elemental silicon or the reaction of silicon

tetrachloride with ammonia (in the gas phase or in solution) for the latter, do not involve soluble or fusible intermediates. For many applications of these materials this is not necessarily a disadvantage (e.g., for the application of SiC as an abrasive), but for some of the more recent desired applications soluble or fusible (i.e., processable) intermediates are required.

The need for soluble or fusible precursors whose pyrolysis will give the desired ceramic material has led to a new area of macromolecular science, that of preceramic polymers [3]. Such polymers are needed for a number of different applications. Ceramic powders by themselves are difficult to form into bulk bodies of complex shape. Although ceramists have addressed this problem using the more conventional ceramics techniques with some success, preceramic polymers could, in principle, serve in such applications, either as the sole material from which the shaped body is fabricated or as a binder for the ceramic powder from which the shaped body is to be made. In either case, pyrolysis of the green body would then convert the polymer to a ceramic material, hopefully of the desired composition. In the latter alternative, shrinkage during pyrolysis should not be great.

Ceramic fibers of diverse chemical compositions are sought for application in the production of metal-, ceramic-, glass- and polymer-matrix composites [3c]. The presence of such ceramic fibers in a matrix, provided they have the right length-to-diameter ratio and are distributed uniformly throughout the matrix, can result in very considerable increases in the strength (i.e., fracture toughness) of the resulting material. To prepare such ceramic fibers, a suitable polymeric precursor is needed, one which can be spun by melt-spinning, dry-spinning, or wet-spinning techniques [4] into fibers which then can be pyrolyzed (with or without a prior cure step).

Some materials with otherwise very useful properties such as high thermal stability and great strength and toughness are unstable with respect to oxidation at high temperatures. An example of such a class of materials is that of the carbon-carbon composites. If these materials could be protected against oxidation by infiltration of their pores and the effective coating of their surface by a polymer whose pyrolysis gives an oxidation-resistant ceramic material, then one would have available new dimensions of applicability of such carbon-carbon composite materials.

In order to have a useful preceramic polymer, considerations of structure and reactivity are of paramount importance. Not every inorganic or

organometallic polymer will be a useful preceramic polymer. Some more general considerations merit discussion. Although preceramic polymers are potentially "high value" products if the desired properties result from their use, the more generally useful and practical systems will be those based on commercially available, relatively cheap starting monomers. Preferably, the polymer synthesis should involve simple, easily effected chemistry which proceeds in high yield. The preceramic polymer itself should be liquid or, if a solid, it should be fusible and/or soluble in at least some organic solvents, i.e., it should be processable. Its pyrolysis should provide a high yield of ceramic residue and the pyrolysis volatiles preferably should be non-hazardous and non-toxic. In the requirement of high ceramic yield, economic considerations are only secondary. If the weight loss on pyrolysis is low, shrinkage will be minimized as will be the destructive effects of the gases evolved during the pyrolysis.

There are important considerations as far as the chemistry is concerned. First, the design of the preceramic polymer is of crucial importance. Many linear organometallic and inorganic polymers, even if they are of high molecular weight, decompose thermally by formation and evolution of small cyclic molecules, and thus the ceramic yield is low. In such thermolyses, chain scission is followed by "back-biting" of the reactive terminus thus generated at a bond further along the chain. Thus high molecular weight, linear poly(dimethylsiloxanes) decompose thermally principally by extruding small cyclic oligomers, $(Me_2SiO)_n$, n = 3,4,5 . . . When a polymer is characterized by this type of thermal decomposition, the ceramic yield will be low and it will be necessary to convert the linear polymer structure to a highly cross-linked one by suitable chemical reactions prior to its pyrolysis. In terms of the high ceramic yield requirement, the ideal preceramic polymer is one which has functional substituent groups which will give an efficient thermal cross-linking process so that on pyrolysis non-volatile, three-dimensional networks (which lead to maximum weight retention) are formed. Thus, preceramic polymer design requires the introduction of reactive or potentially reactive functionality.

In the design of preceramic polymers, achievement of the desired elemental composition in the ceramic obtained from them (SiC and Si_3N_4 in the present cases) is a major problem. For instance, in the case of polymers aimed at the production of SiC on pyrolysis, it is more usual than not to obtain solid residues after pyrolysis which, in addition to SiC, contain an excess either

of free carbon or free silicon. In order to get close to the desired elemental composition. two approaches have been found useful in our research: (1) The use of two comonomers in the appropriate ratio in preparation of the polymer. and (2) the use of chemical or physical combinations of two different polymers in the appropriate ratio.

Preceramic polymers intended for melt-spinning require a compromise. If the thermal cross-linking process is too effective at relatively low temperatures (100-200°C). then melt-spinning will not be possible since heating will induce cross-linking and will produce an infusible material prior to the spinning. A less effective cross-linking process is required so that the polymer forms a stable melt which can be extruded through the holes of the spinneret. The resulting polymer fiber. however. must then be "cured". i.e.. cross-linked. chemically or by irradiation. to render it infusible so that the fiber form is retained on pyrolysis. Finally. there still are chemical options in the pyrolysis step. Certainly. the rate of pyrolysis. i.e.. the time/temperature profile of the pyrolysis. is extremely important. However. the gas stream used in the pyrolysis also is of great importance. One may carry out "inert" or "reactive" gas pyrolyses. An example of how one may in this way change the nature of the ceramic product is provided by one of our preceramic polymers which will be discussed in more detail later in this paper. This polymer. of composition $[(CH_3SiHNH)_a(CH_3SiN)_b]_m$. gives a <u>black</u> solid. a mixture of SiC. Si_3N_4. and some free carbon. on pyrolysis to 1000°C in an inert gas stream (nitrogen or argon). However. when the pyrolysis is carried out in a stream of ammonia. a <u>white</u> solid remains which usually contains less than 0.5% total carbon and is essentially pure silicon nitride. At higher temperatures (>400°C). the NH_3 molecules effect nucleophilic cleavage of the Si-C bonds present in the polymer and the methyl groups are lost as CH_4. Such chemistry at higher temperatures can be an important and sometimes useful part of the pyrolysis process.

The first useful organosilicon preceramic polymer. a silicon carbide fiber precursor. was developed by S. Yajima and his coworkers at Tohoku University in Japan [5]. As might be expected on the basis of the 2 C 1 Si ratio of the $(CH_3)_2SiCl_2$ starting material used in this process. the ceramic fibers contain free carbon as well as silicon carbide. A typical analysis [5] showed a composition 1 SiC/0.78 C/0.22 SiO_2. (The latter is introduced in the oxidative cure step of the polycarbosilane fiber).

The Yajima polycarbosilane. while it was one of the first. is not the only polymeric precursor to silicon carbide which has been developed. Another useful system which merits mention is the polycarbosilane which resulted from research carried out by C. L. Schilling and his coworkers in the Union Carbide Laboratories in Tarrytown. New York [6]. More recently. a useful polymeric precursor for silicon nitride has been developed by workers at Dow Corning Corporation [7].

## NEW SILICON-BASED PRECERAMIC POLYMER SYSTEMS: RECENT RESEARCH AT M.I.T.

In earlier work [8]. we have developed a process for the preparation of useful preceramic polymers using commercially available CH_3SiHCl_2 as the starting material. In the initial step. this chlorosilane was treated with ammonia to give oligomeric. mostly cyclic $[CH_3SiHNH]_n$ (n~5). This product. itself not a useful preceramic material. was subjected to the base-catalyzed dehydrocyclodimerization (DHCD) reaction (eq. 1) in which the species present in the $[CH_3SiHNH]_n$ oligomer mixture are linked together via cyclodisilazane units.

$$2 \ -Si-N- \quad \xrightarrow[\text{(e.g.. KH)}]{\text{base}} \quad H_2 + \ \text{Si} \overset{N}{\underset{N}{\diagdown}} \text{Si} \qquad (1)$$
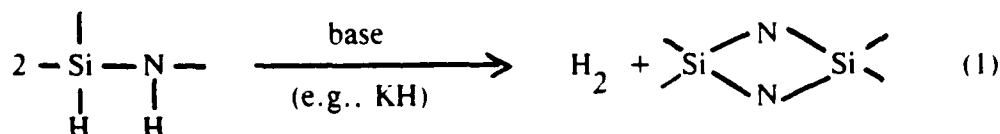
The repeating unit in the $[CH_3SiHNH]_n$ cyclics is 1.
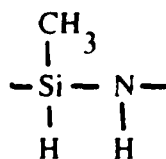
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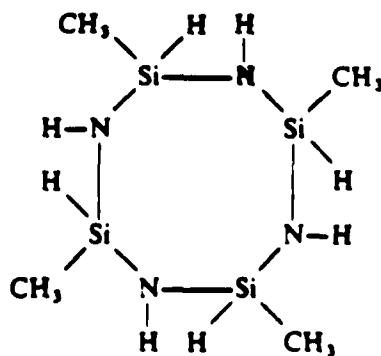
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For example. the cyclic tetramer is the 8-membered ring compound $\underline{2}$. On the basis of equation 1. the adjacent NH and SiH groups provide the functionality which permits the molecular weight of the $[CH_3SiHNH]_n$ cyclics to be increased. Thus. $[CH_3SiHNH]_n$ cyclics will be linked together via four-membered rings as shown in $\underline{3}$.

R = CH₃
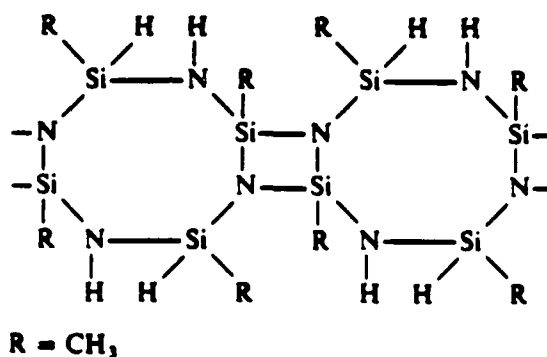
$\underline{3}$

We believe that a sheet-like network polymer (which. however. is not flat) having the general functional unit composition $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]_n$ results. When hydrogen evolution ceases. a "living" polymer with reactive silylamide functions is present. On reaction of the latter with an electrophile (CH_3I or a chlorosilane). the neutral polysilazane is formed and can be isolated in the form of an organic-soluble white solid when the reaction is carried out in THF solution. Depending on solvent and reaction conditions. the molecular weight of this product is between 800 and 2500 g/mol. The molecular weight can be approximately doubled by using a difunctional chlorosilane (such as $ClMe_2SiCH_2CH_2SiMe_2Cl$) to quench the "living" polymer. Such polysilazanes. when pyrolyzed in a stream of argon. leave behind a black ceramic residue equivalent to 80-85% of the weight of the originally charged polymer. Analysis gave % Si. C and N values which could be rationalized in terms of a composition of (by weight) 67% Si_3N_4. 28% SiC and 5% C. The volatiles evolved during the pyrolysis consisted of H_2

and CH_4 and a trace of NH_3. Initial evaluation of the polysilazane shows it to have promise in three of the main potential applications of preceramic polymers: in the preparation of ceramic fibers and of ceramic coatings and as a binder for ceramic powders.

This polysilazane undergoes thermal crosslinking too readily to permit melt-spinning. but it can be dry-spun. It was clear that if melt-spinning was to be successful we would have to prepare a less reactive polysilazane with fewer reactive Si(H)-N(H) groups. To achieve this. we have studied polysilazanes derived by the dehydrocyclodimerization of the products of coammonolysis of CH_3SiHCl_2 and $CH_3(Un)SiCl_2$. where Un is an unsaturated substituent such as vinyl. $CH_2=CH$. or allyl. $CH_2CH=CH_2$. These groups were used because a melt-spun fiber requires a subsequent cure step to render it infusible. If this is not done. the fiber would simply melt on pyrolysis and no ceramic fiber would be obtained. The vinyl and allyl groups provide $C=C$ functionality which can undergo UV-catalyzed Si-H additions. reactions which after melt-spinning in principle should lead to extensive further crosslinking without heating.

To provide the required monomers. we ammonolyzed mixtures of CH_3SiHCl_2 and $CH_3(CH_2=CH)SiCl_2$ and CH_3SiHCl_2 and $CH_3(CH_2=CHCH_2)SiCl_2$. respectively. The $[(CH_3SiHNH)_x(CH_3(Un)SiNH)_y]_n$ oligomers were prepared using $CH_3SiHCl_2/CH_3(Un)SiCl_2$ ratios of 3. 4 and 6. although other ratios can be used. This gives materials which still contain many $(CH_3)Si(H)$-N(H)- units. so polymerization by means of the process of eq. 1 still will be possible. However. dilution of the ring systems of the cyclic oligomers with $CH_3(Un)Si$ units will decrease the cross-linking which will occur on treatment with the basic catalyst.

The coammonolysis of CH_3SiHCl_2 and $CH_3(Un)SiCl_2$ in the indicated ratios was carried out by the procedure as described for the ammonolysis of CH_3SiHCl_2 [8]. A mixture of cyclic oligomeric silazanes is to be expected in these reactions. $[(CH_3(H)SiNH)_x(CH_3(Un)SiNH)_y]_n$. with more than one ring size present. In each preparation. the soluble. liquid products were isolated and used in the base-catalyzed polymerizations. When a ratio $CH_3SiHCl_2/CH_3(Un)SiCl_2$ of x:1 (x > 1) was used in the ammonolysis reaction. the $CH_3(H)Si/CH_3(Un)Si$ ratio in the soluble ammonolysis product usually was somewhat less than x:1.

The addition of the various ammonolysis products to suspensions of catalytic amounts of KH in dry tetrahydrofuran resulted in hydrogen gas

evolution with formation of a clear solution. Thermal treatment was followed by treatment with methyl iodide to "kill" the "living" polymeric potassium silylamide present in solution. The resulting silazane generally was obtained in high (>90%) yield and these products. always white powders. were soluble in organic solvents such as hexane. benzene. toluene and THF. Their average molecular weights were in the 800 - 1200 range. The presence of unchanged vinyl and allyl groups was proven by their IR and ^{1}H NMR spectra. A typical elemental analysis led to the empirical formula $SiC_{1.5}NH_{4.4}$ which could be translated into a composition $[(CH_3SiHNH)(CH_3\{CH_2=CH\}SiNH)_{2.3}]_x$.

These polysilazanes. upon pyrolysis to 1000°C under argon or nitrogen. gave black ceramic materials in good yield (73-86%. by weight). Analysis of the ceramic produced by such pyrolysis of one of these polysilazanes gave a composition 67.5 wt.% Si_3N_4. 22.5 wt.% SiC. and 10.0 wt.% unbound carbon. Another such ceramic sample. obtained by pyrolysis of another polysilazane. had the composition 68.8 wt% Si_3N_4. 21.7 wt.% SiC. and 9.9 wt.% C.

The possibility of "curing" fibers pulled from polysilazanes of the type prepared here was demonstrated in the following experiment: Fibers were pulled from a concentrated syrup of a polysilazane derived from a 4:1 molar ratio $CH_3SiHCl_2/CH_3(CH_2=CH)SiCl_2$ coammonolysis product by DHCD in THF. Some fibers were pyrolyzed without any further treatment. These melted in large part. leaving very little in the way of ceramic fibers. Other fibers were subjected to UV irradiation for 2 hours. These. on pyrolysis under argon. did not melt and ceramic fibers were obtained. This polysilzane then is a good candidate for melt-spinning.

In order to obtain a SiC/Si_3N_4 mixture rich in Si_3N_4 by the preceramic polymer route. one requires a polymer which is richer in nitrogen than the CH_3SiHCl_2 ammonolysis product. $(CH_3SiHNH)_n$. In designing such a preceramic polymer. one would like to retain the facile chemical and thermal cross-linking system which the Si(H)-N(H)-unit provides. We have found that the coammonolysis of CH_3SiHCl_2 and $HSiCl_3$ serves our purposes well. For $HSiCl_3$. ammonolysis introduces three Si-N bonds per silicon atom. so the ammonolysis product of CH_3SiHCl_2 $HSiCl_3$ mixtures will contain more nitrogen than the ammonolysis product of CH_3SiHCl_2 alone.

In order to define the optimum system. we have investigated the ammonolysis of CH_3SiHCl_2 $HSiCl_3$ mixtures in various ratios in two solvents.

diethyl ether. Et_2O. and tetrahydrofuran. THF. $CH_3SiHCl_2/HSiCl_3$ mol ratios of 6. 3 and 1 were examined.

In both solvents. the 6:1 and 3:1 ratios produced polysilazane oils with molecular weights in the range 390-401 g/mol and 480 g/mol. respectively. When a 1:1 reactant ratio was used. waxes of somewhat higher (764-778 g/mol) molecular weights were obtained in both solvents. In the 1:1 reaction carried out in Et_2O the yield of soluble product was only 40%. but in THF it was nearly quantitative.

The oils produced in the 6:1 and 3:1 reactions in Et_2O appeared to be stable on long-term storage at room temperature in the absence of moisture (e.g.. in the inert atmosphere box). However. the waxy product of 1:1 (Et_2O) reactions and all the coammonolysis products prepared in THF formed gels (i.e.. became insoluble) after 3-4 weeks at room temperature. even when stored in a nitrogen-filled dry box.

The pyrolysis of the coammonolysis products was studied. The 6 $CH_3SiHCl_2/1$ $HSiCl_3$ ammonolysis product would be the least cross-linked since it contains the least amount of trifunctional component and. as expected. low ceramic yields were obtained on pyrolysis of these products. Pyrolysis of the 3:1 products gives increased ceramic yields. while pyrolysis of the most highly cross-linked 1:1 ammonolysis products gives quite good ceramic yields. 72% for the product prepared in Et_2O. 78% for that prepared in THF.
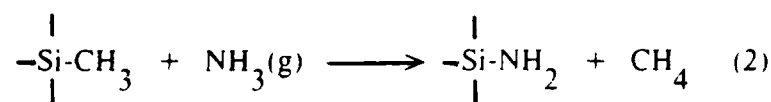
All of the ammonolysis products were submitted to the KH-catalyzed dehydrocyclodimerization reaction in order to obtain more highly cross-linked products that would give higher ceramic yields on pyrolysis. In all cases. the standard procedure [8] was used (1% KH in THF. followed by quenching with CH_3I (or a chlorosilane)). In every reaction. the product was a white solid which was produced in virtually quantitative yield. The proton NMR spectra of these products. as expected. showed an increase in the $SiCH_3/SiH + NH$ proton ratio. while the relative SiH/NH ratio was unchanged. In all cases. the molecular weights of the solid products were at least double that of the starting ammonolysis product. so the desired polymerization had occurred. Although the increase in molecular weight in these DHCD reactions is not great. any increase is useful for further processing. The reactions bring the advantage that the oils are converted to more easily handleable solids.

Pyrolysis of the white solids obtained in these KH-catalyzed dehydrocyclodimerization reactions (under argon from 50-950°C) produced

black ceramic residues. with the exception of the 1:1 THF ammonolysis-derived solid which left a brown residue. The ceramic yields were excellent (all greater than or equal to 82%. with the highest being 88%).

Analysis of bulk samples of the ceramic materials produced in the pyrolysis of the various KH-catalyzed dehydrocyclodimerization products showed that our goal of a higher Si_3N_4/SiC ratio has been achieved: for the 1:1 ammonolysis product-derived polymers. 86% Si_3N_4. 8% SiC and 5% C (THF ammonolysis) and 83% Si_3N_4. 11% SiC and 6% C (Et_2O ammonolysis): for the 3:1 and 6:1 ammonolysis product-derived polymers: 77% Si_3N_4. 18-19% SiC and 4-5% C (Et_2O ammonolysis) and 74% Si_3N_4. 20% SiC and 5-6% C (THF ammonolysis).

These polymers may be used in the preparation of quite pure silicon nitride if the pyrolysis is carried out in a stream of ammonia (a reactive gas) rather than under nitrogen or argon. The ammonia reacts with the polymer at higher temperatures to cleave methyl groups from silicon (eq. 2). so that essentially all carbon is lost. Thus. pyrolysis of the

$$\begin{matrix} | \\ -Si\text{-}CH_3 \\ | \end{matrix} + NH_3(g) \longrightarrow \begin{matrix} | \\ -Si\text{-}NH_2 \\ | \end{matrix} + CH_4 \quad (2)$$

dehydrocyclodimerization product of the 1:1 (THF) ammonolysis product to 1000°C in a stream of ammonia gave a white ceramic residue in high yield which contained only 0.29% C. the remainder being silicon nitride.

Other commercially available $RSiCl_3$ compounds are CH_3SiCl_3 (a cheap by-product of the Direct Process) and $CH_2=CHSiCl_3$ (also an inexpensive starting material) and both were included in this study. In both cases. 6:1. 3:1 and 1:1 CH_3SiHCl_2/$RSiCl_3$ ammonolysis products were prepared and submitted to the dehydrocyclodimerization procedure. The ceramic yields obtained on pyrolysis of the resulting polymers were high. In the CH_3SiHCl_2 CH_3SiCl_3 experiments: 78-86%. In all cases. a black ceramic residue resulted when the pyrolysis to 1000°C was carried out in a stream of argon. As expected. the carbon content (in the form of SiC and free C) was higher than that of the CH_3SiHCl_2 $HSiCl_3$-derived ceramics: 12-18% SiC. up to 9.5% C. Nonetheless. higher Si_3N_4 contents than those obtained when CH_3SiHCl_2 is used alone (~67%) were obtained: ~76-80% Si_3N_4.

To produce a ceramic material containing only Si_3N_4. the white solid polysilazane derived from DHCD of the oil obtained by ammonolysis of 6:1

CH_3SiHCl_2/CH_3SiCl_3 was pyrolyzed in a stream of ammonia (to 1000°C). A white ceramic residue containing only 0.36% by weight C resulted.

With 6:1. 3:1 and 1:1 $CH_3SiHCl_2/CH_2=CHSiCl_3$ ammonolysis products DHCD gave white solids whose pyrolysis resulted in increased carbon content and decreased Si_3N_4 (vs the CH_3SiHCl_2/CH_3SiCl_3 examples): ~69-73% Si_3N_4. 9-13% SiC. 12-18% C (by weight).

Our research also has been directed at SiC precursors. It began with an examination of a potential starting material in which the C:Si ratio was 1, the ratio desired in the derived ceramic product. Available methylsilicon compounds with a 1 C/1 Si stoichiometry are CH_3SiCl_3 and CH_3SiHCl_2. The latter. in principle. could give $[CH_3SiH]_n$ cyclic oligomers and linear polymers on reaction with an alkali metal. In practice. the Si-H linkages also are reactive toward alkali metals. Thus. mixed organochlorosilane systems containing some CH_3SiHCl_2 have been treated with metallic potassium by Schilling and Williams [9]. It was reported that the CH_3SiHCl_2-based contribution to the final product was $(CH_3SiH)_{0.2}(CH_3Si)_{0.8}$. i.e.. about 80% of the available Si-H bonds had reacted. Such Si-H reactions lead to cross-linking in the product. or to formation of polycyclic species if cyclic products are preferred. Nevertheless. we have used this known reaction of CH_3SiHCl_2 with an alkali metal as an entry to new preceramic polymers.

When the reaction of CH_3SiHCl_2 with sodium pieces was carried out in tetrahydrofuran medium. a white solid was isolated in 48% yield. This solid was poorly soluble in hexane. somewhat soluble in benzene. and quite soluble in THF. Its ^{1}H NMR spectrum (in $CDCl_3$) indicated that extensive reaction of Si-H bonds had occurred. The $\delta(SiH)/\delta(SiCH_3)$ integration led to a constitution $[(CH_3SiH)_{0.4}(CH_3Si)_{0.6}]_n$. Here the CH_3SiH units are ring and chain members which are not branching sites: the CH_3Si units are ring and chain members which are branching sites. In our reactions it is expected that mixtures of polycyclic and linear (possibly cross-linked) polysilanes will be formed. (Attempts to distill out pure compounds from our preparations were not successful. Less than 10% of the product was volatile at higher temperatures at 10^{-4} torr.). The ceramic yield obtained when the $[(CH_3SiH)_{0.4}(CH_3Si)_{0.6}]_n$ polymer was pyrolyzed (TGA to 1000°C) was 60%: a gray-black solid was obtained whose analysis indicated a composition 1.0 SiC + 0.49 Si.

The reaction of methyldichlorosilane with sodium in a solvent system composed of six parts of hexane and one of THF gave a higher yield of product which was soluble in organic solvents. Such reactions give a colorless oil in 75 to over 80% yield which is soluble in many organic solvents. In various experiments the molecular weight (cryoscopic in benzene) averaged 520-740 and the constitution (by ^{1}H NMR) $[(CH_3SiH)_{0.76}(CH_3Si)_{0.24}]_n$ to $[(CH_3SiH)_{0.9}(CH_3Si)_{0.1}]_n$. This less cross-linked material (compared to the product obtained in THF alone) gave much lower yields of ceramic product on pyrolysis to 1000°C (TGA yields ranging from 12-27% in various runs). Again. the product was (by analysis) a mixture of SiC and elemental silicon. 1.0 SiC + 0.42 Si being a typical composition. These results are not especially promising. and it was obvious that further chemical modification of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ products obtained in the CH_3SiHCl_2 Na reactions was required [10].

A number of approaches which we tried did not lead to success. but during the course of our studies we found that treatment of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ products with alkali metal amides (catalytic quantities) serves to convert them to materials of higher molecular weight whose pyrolysis gives significantly higher ceramic yields. Thus. in one example. to 0.05 mol of liquid $[(CH_3SiH)_{0.85}(CH_3Si)_{0.15}]$ in THF was added. under nitrogen. a solution of about 1.25 mmol (2.5 mol%) of $[(CH_3)_3Si]_2NK$ in THF. The resulting red solution was treated with methyl iodide. Subsequent nonhydrolytic workup gave a soluble white powder in 68% yield. molecular weight 1000. whose pyrolysis to 1000°C gave a ceramic yield of 63%.

The proton NMR spectra of this product showed only broad resonances in the Si-H and Si-CH$_3$ regions. In the starting $[(CH_3SiH)_x(CH_3Si)_y]_n$ material. the observed proton NMR integration ratios. SiCH$_3$ SiH. ranged from 3.27-3.74. This ratio was quite different in the case of the product of the silylamide-catalyzed process. ranging from 8.8 to 14. Both Si-H and Si-Si bonds are reactive toward nucleophilic reagents. In the case of the alkali metal silylamides. extensive structural reorganization. involving both Si-H and Si-Si bonds of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilane. that results in further cross-linking. must have taken place.

While these silylamide-catalyzed reactions provided a good way to solve the problem of the low ceramic yield in the pyrolysis of $[(CH_3SiH)_x(CH_3Si)_y]_n$. the problem of the elemental composition of the

ceramic product remained (i.e.. the problem of Si/C ratios greater than one) since only catalytic quantities of the silylamide were used.

As noted above. KH-catalyzed polymerization of the CH_3SiHCl_2 ammonolysis product gives a polymeric silylamide of type $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]$. In a typical example. a = 0.39. b = 0.57. c = 0.04. so there is only a low concentration of silylamide functions in the polymer. This polymeric silylamide reacts with electrophiles other than methyl iodide. e.g.. with diverse chlorosilanes. and it has been isolated and analyzed. Since it is a silylamide. we expected that it also would react with $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilane-type materials. Not only would it be expected to convert the latter into material of higher molecular weight. but it also would be expected to improve the Si/C ratio (i.e.. bring it closer to 1). As noted above. pyrolysis of $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNCH_3)_c]_n$ gives a ceramic product in 80-85% yield containing Si_3N_4. SiC and excess carbon. Thus. combination of the two species in the appropriate stoichiometry. i.e.. of $[(CH_3SiH)_x(CH_3Si)_y]_n$ and $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]_n$. and pyrolysis of the product (which we will call a "graft" polymer) after CH_3I quench could. in principle. lead to a ceramic product in which the excess Si obtained in pyrolysis of the former and the excess C obtained in the pyrolysis of the latter combine to give SiC. Accordingly. experiments were carried out in which the two polymer systems. $[(CH_3SiH)_x(CH_3Si)_y]_n$ and the "living" polymer-silyl amide. $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]_n$. were mixed in THF solution in varying proportions (2.4:1 to 1:2 mole ratio) and allowed to react at room temperature for 1 h and at reflux for 1 h. (Such experiments were carried out with the $[(CH_3SiH)_x(CH_3Si)_y]_n$ materials prepared in hexane/THF as well as with those prepared in THF alone.) After quenching with methyl iodide. nonhydrolytic workup gave a new polymer in nearly quantitative yield (based on weight of material charged). The molecular weight of these products was in the 1800-2500 range. Their pyrolysis under nitrogen gave ceramic products in 74-83% yield. Thus. the reaction of the two polymer systems gives a new polymer in close to quantitative yield which seems to be an excellent new preceramic polymer in terms of ceramic yield.

In an alternative method of synthesis of $[(CH_3SiH)_x(CH_3Si)_y][(CH_3SiHNH)_a(CH_3SiN)_b]$ "combined" polymers. the polysilyl amide was generated in situ in the presence of $[(CH_3SiH)_x(CH_3Si)_y]_n$. This. however. gave materials that were somewhat different. In one such

experiment. a mixture of $(CH_3SiHNH)_n$ cyclics (as obtained in the ammonolysis of CH_3SiHCl_2 in THF) and the $[(CH_3SiH)_x(CH_3Si)_y]_n$ material (x = 0.76; y = 0.26) in THF was treated with a catalytic amount of KH. After the reaction mixture had been treated with methyl iodide. the usual workup gave an 89% yield of hexane-soluble white powder. molecular weight ~2750. On pyrolysis. this material gave a 73% yield of a black ceramic.

The "combined" polymer prepared in this way ("in situ polymer") was in some ways different from the "combined" polymer prepared by the first method ("graft" polymer). Principal differences were observed in their proton NMR spectra and in the form of their TGA curves. This suggests that the two differently prepared polymers have different structures. It is likely that in the "in situ" preparation intermediates formed by the action of KH on the $(CH_3SiHNH)_n$ cyclics are intercepted by reaction with the $[(CH_3SiH)_x(CH_3Si)_y]_n$ also present before the $[(CH_3SiHNH)_a(CH_3SiH)_b(CH_3SiHNK)_c]_n$ polymer (which is the starting reactant used in the "graft" procedure) has a chance to be formed to the extent of its usual molecular weight. Thus. less of the original $CH_3Si\underline{H}NH$ protons are lost and/or more of those of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ system are reacted.

The TGA curves of the "graft" polymer and the "in situ" polymer are different as well. Noteworthy in the former is a small weight loss between 100°C and 200°C. which begins at around 100°C. This initial small weight loss occurs only at higher temperature (beginning at ~175°C) in the case of the "in situ" polymer. This difference in initial thermal stability could well have chemical consequences of importance with respect to ceramics and both kinds of polymers may be useful as preceramic materials.

Further experiments showed that the "combined" polymers may be converted to black ceramic fibers. Pyrolysis of pressed bars of the "combined polymer to 1000°C gave a black product of irregular shape (74-76% ceramic yield). In other experiments. SiC powder was dispersed in toluene containing 20% by weight of the "combined" polymer. The solution was evaporated and the residue. a fine powder of SiC with the "combined" polymer binder. was pressed into bars and pyrolyzed at 1000°C. A ceramic bar (6% weight loss. slightly shrunk in size) was obtained.

The ceramic products obtained in the pyrolysis of the "combined" polymers have not been studied in detail. but some of them have been analyzed for C. N. and Si. The compositions of the ceramic materials obtained cover the

range 1 Si_3N_4 + 3.3 to 6.6 SiC + 0.74 to 0.85 C. Thus. as expected, they are rich in silicon carbide and the excess Si which is obtained in the pyrolysis of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ materials alone is not present. so that objective has been achieved. By proper adjustment of starting material ratios. we find that the excess carbon content can be minimized [11].

The "living polymer" intermediate in our polysilazane synthesis is useful in "upgrading" other Si-H containing polymers for application as precursors for ceramic materials. Another example of this application is provided by such "upgrading" of methylhydrogenpolysiloxane. $[CH_3Si(H)O]_n$. Such a linear polymer. average molecular weight 2000-5000 (vendor data). on pyrolysis under argon to 1000°C. left a black ceramic residue of only 13%.

In this study. experiments were carried out with a $[CH_3Si(H)O]_m$ prepared using conditions under which the yield of the cyclic oligomers (m = 4. 5. 6. ....) is maximized [12]. as well as with the commercial $[CH_3Si(H)O]_m$ polymer of higher molecular weight. with presumably high linear content.

In one approach. the polymeric silylamide was prepared as described above (using the product of CH_3SiHCl_2 ammonolysis in THF) and to this "living" polymer solution were added slowly the $[CH_3Si(H)O]_m$ oligomers (high cyclic content). An immediate reaction with some gas evolution occurred. The resulting clear solution was treated with CH_3I to react with any remaining silylamide or silanolate units. Silylamide/siloxane weight ratios of 1:1 and 1:5 were used. In both cases the polymeric product was an organic-soluble white solid of moderate (1700 and 2400. respectively) average molecular weight. In both cases pyrolysis under nitrogen or argon gave high char yields (78% and 76%. respectively. by TGA). Pyrolysis to 1000°C of a bulk sample of the 1:1 by weight polymer gave a black solid in 80% yield. Elemental analysis indicated a "composition": 1 SiC + 0.84 Si_3N_4 + 2.17 SiO_2 + 2.0 C. (This is not meant to reflect the composition in terms of chemical species present. No doubt. rather than separate Si_3N_4 and SiO_2. silicon oxynitrides are present). On the other hand. pyrolysis under gaseous ammonia gave a white ceramic solid in 78.5% yield. It is suggested that here also high temperature nucleophilic cleavage of Si-CH_3 bonds by NH_3 occurred and that the ceramic product is a silicon oxynitride. This was confirmed by analysis. The white solid contained less than 0.5% carbon.

In an alternate approach to this "graft" procedure. the "in situ" procedure was used. A mixture (~1:1 by weight) of the CH_3SiHCl_2 ammonolysis (in

THF) product. $[CH_3SiHNH]_m$. and the CH_3SiHCl_2 hydrolysis product.
$[CH_3Si(H)O]_n$. in THF. was added to a suspension of a catalytic amount of KH
in THF. Hydrogen evolution was observed and a clear solution resulted. After
quenching with CH_3I. further work-up gave the new polymer a soluble white
powder. average molecular weight 1670. Pyrolysis to 1000°C gave a black
ceramic solid in 84% yield (by TGA). Pyrolysis of a bulk sample under argon
yielded a black ceramic (73%). Analysis indicated the "composition": 1 SiC +
1.03 Si_3N_4 + 1.8 SiO_2 + 2.63 C.

In place of the (mostly) cyclic $[CH_3SiHO]_n$ oligomers. a commercial
methylhydrogenpolysiloxane (Petrarch PS-122) of higher molecular weight.
presumably mostly linear species. may serve as the siloxane component. When
a 1:1 by weight ratio of the preformed polymeric silylamide and the
$[CH_3Si(H)O]_n$ polymer was used and the reaction mixture was quenched with
CH_3I. the usual work-up produced a soluble white solid. molecular weight
1540. Pyrolysis under argon to 1000°C gave a black ceramic material (77%
yield by TGA). Pyrolysis of a bulk sample yielded a black solid (73% yield)
whose analysis indicated a "composition": 1 SiC + 1.5 Si_3N_4 + 3.15 SiO_2 +
3.6 C. Application of the "in situ" procedure [1:1 by weight ratio of
$(CH_3SiHNH)_m$ and $[CH_3Si(H)O_n]$ gave a soluble white powder. average
molecular weight 1740. pyrolysis yield (TGA) 88% (black solid). The fact that
the pyrolysis of these polymers under a stream of ammonia gives white solids.
silicon oxynitrides which contain little. if any. carbon. in high yield is of
interest. The ceramics applications of these silicon oxynitride precursor systems
are receiving further study by Yu and Ma of Universal Energy Systems [13].

The chemistry which is involved in the "graft" and "in situ" procedures
and the structures of the hybrid polymers which are formed remain to be
elucidated. However. there is no doubt that these procedures are useful ones.
We have used them also to form new and useful hybrid preceramic polymers
from the Yajima polycarbosilane (which contains a plurality of $[CH_3Si(H)CH_2]$
units [14].

CONCLUSIONS

We have described new routes to useful preceramic organosilicon polymers and have demonstrated that their design is an exercise in functional group chemistry. Furthermore, we have shown that an organosilicon polymer which seemed quite unpromising as far as application is concerned could, through further chemistry, be incorporated into new polymers whose properties in terms of ceramic yield and elemental composition were quite acceptable for use as precursors for ceramic materials. It is obvious that the chemist can make a significant impact on this area of ceramics. However, it should be stressed that the useful applications of this chemistry can only be developed by close collaboration between the chemist and the ceramist.

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